



Country report

Heavy metals, PAHs and POPs in recycled polyethylene samples of agricultural, post-commercial, post-industrial and post-consumer origin

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ARTICLE INFO

Keywords:

Dioxins
 Furans
 Dioxin-like PCBs
 Plastic waste
 Post-consumer waste
 Post-industrial waste

ABSTRACT

In the present work, recycled polyethylene (LDPE) samples of agricultural, post-commercial, post-industrial and post-consumer origin were selected and analysed. The analysis comprised the determination of different contaminants such as metals, polycyclic aromatic hydrocarbons (PAHs), dioxin-like biphenyl polychlorides (PCBs), and polychlorinated-dibenzo-p-dioxins and furans (PCDD/Fs). A comparison with one sample of virgin plastic (unrecycled) was performed. The study aimed at stressing the importance of this type of analysis in recycled plastics. Indeed, such an examination will determine the material's final destination, and the possible origin of the pollutants analysed is investigated. Black post-industrial and post-consumer samples presented the highest concentration of PCBs and PCDD/Fs, attaining a maximum value of 2.40 pg WHO-TEQ/g, while the least toxic sample (post-commercial) presented a toxicity of 0.38 pg WHO-TEQ/g. PAHs content was also much higher in black samples, reaching 514.41 ng/g, while the lowest concentrations were obtained for the post-commercial plastic sample, which did not exceed 38.98 ng/g. The higher PAHs concentrations in the black samples were related to the carbon black content of the black samples, which was 2.00% for black post-industrial sample and 1.51% for post-consumer sample. The PCDD/Fs congener profile observed in almost all samples was very similar to the profile found in the literature on urban air samples, indicating that the plastic is mainly influenced by the environment. The presence of some metals (mainly copper) showed a slight correlation with PCDD/Fs content. The pollutants analysed were found to be significantly reduced during the cleaning processes that are generally carried out in recycling companies.

1. Introduction

Plastics are currently improving the quality of life of people all over the world. Nevertheless, the full potential of plastics cannot be appreciated if we do not address and solve problems deriving from their negative environmental impact. Therefore, innovative and sustainable solutions must be developed to boost the circular economy of plastics.

Currently, 60% of products generated from plastic have a useful life of 1–50 years, after which they turn into waste and have negative effects. In 2018, some 359 million tons of plastic were generated worldwide (16% of that total was produced in Europe), of which only 29.1 million tons were collected for further treatment: energy recovery (42.6%), recycling (32.5%), and landfill (24.9%). These figures indicate that only 9.4 million tons of post-consumer plastic waste were recycled globally.

Among these products, the most sought-after plastics are polyolefins (PS, LDPE, LLDPE, HDPE, and MDPE), which, in 2019, generated a total demand of >24 million tons. The amount of plastic being recycled is increasing, with 50% more plastic being recycled in 2020 than in 2006 (PlasticEurope-Association of Plastics Manufactures, 2020).

With respect to the most demanded plastics, the uses of polyolefins vary widely and include food packaging, reusable bags, films for food packaging, toys and milk bottles, among others (PlasticEurope-Association of Plastics Manufactures, 2020). Most of these plastics, therefore, enter the composition of products for human consumption and must have very high quality standards, which makes it difficult to recycle them, i.e. to be used for the same purpose as the original product (European Union, 2011).

To counteract the negative environmental effects of plastics, the

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European Union Waste Framework Directive 2008/98/EC7 established a waste hierarchy to be applied in order of priority in legislation and waste prevention and management. The aim is to reduce waste through the reuse and recycling of plastics (European Parliament, 2018). Recycling was classified into four categories (ISO 15270:2008) (ASTM D7209). *Primary recycling*, which consists of converting waste through extrusion while maintaining identical physical and chemical properties with respect to the original material. This type of recycling is also called closed-loop recycling or upcycling. Primary recycling presents limitations such as the recycling of mixed plastics (Hopewell et al., 2009), so this process is applied to pre-consumer plastics. In the next category, *secondary or mechanical recycling*, plastic waste is recovered through mechanical processes in such a way that the resulting material can replace virgin polymers or part of them. They generate, however, articles with properties that are inferior to those of the original material (European Commission, 2019). This type of recycling is also called open-cycle recycling or downcycling. On the other hand, in *tertiary recycling*, the polymers are degraded and broken down into basic chemical compounds from polymer chains, so they can be used as raw materials in the production of fuels, other polymers or new chemical products. Finally, *quaternary recycling* consists of energy recovery or the production of electricity and heat by incinerating plastic waste.

The reuse of recycled plastic through primary or secondary recycling represents a more efficient use of resources, as these two types of recycling contribute to a circular economy.

A very important aspect to consider in the recycling of plastics is the number of additives contained in the plastics. They have been extensively studied in the literature. These additives are called Intentionally Added Substances (IAS) and contribute to improve the physico-chemical properties of the plastics. These additives include flame retardants, plasticisers, stabilisers (such as heavy metals) among others (Wagner and Schlummer, 2020), and many authors, such as Hahladakis et al (2018) have studied the migration capacity of these additives during their use, their recycling, and their environmental impact.

But IAS are not the only problem. Other types of hazardous substances should be determined, and their migration capacity studied. These other types of substances are usually called Non-Intentionally Added Substances (NIAS) (Horodytska et al., 2020). The presence of NIAS in recycled materials would indicate that their possible uses would be less demanding in terms of performance compared to the original material (secondary recycling) (European Commission, 2019).

Some authors have analysed samples of recycled plastics searching for NIAS. They have found and classified over 100 volatile organic compounds (VOCs), most coming from cosmetic product additives, together with over 30 semi-volatile compounds in LDPE and HDPE samples (Horodytska et al., 2020). Furthermore, other authors have stressed the importance of considering the possible presence of polycyclic aromatic hydrocarbons (PAHs) and persistent organic compounds (POPs) in recycled material (Conesa et al., 2021), as they are understood to be cancer-causing compounds (Horodytska et al., 2020) (Cabanes et al., 2020).

PAHs are a group of persistent organic compounds generated during the incomplete combustion of biomass and fossil fuels. As pollutants, they have raised concerns among researchers because the substances have been identified as carcinogenic, mutagenic, and teratogenic. These conclusions are supported by various organisations, such as the US Environmental Protection Agency (EPA) and the EU Scientific Committee for Food (SCF) (U.S. EPA, 2013).

Authors such as Li et al (2017) conducted a study on PAHs concentration in polystyrene samples in contact with food. The authors found concentrations ranging from undetectable amounts to 273 ng/g. In another study, Alassali et al (2020) showed that PAHs could be formed during the production and reprocessing of different polyethylene (PE) samples.

Moreover, due to their physical and chemical properties, the POPs group of compounds can remain intact for years once they are released

into the environment. They tend to accumulate in the fatty tissues of living beings. POPs can be divided into two groups: 'legacy' POPs, which have long been recognised as harmful, and 'emerging' POPs, which are now starting to be banned (U.N.E.P., 2002). The 'legacy' group includes different pesticides and dioxin-like compounds such as dioxins (PCDDs), furans (PCDFs) and dioxin-like biphenyls (PCBs). Together with PAHs, all these substances are hazardous for both the environment and human health.

Highly chlorinated compounds from different POPs have previously been shown to have a high affinity with PE-like polyolefins (Bouhroum et al., 2019). No evidence, however, of the presence of PCDD/Fs or PCBs in recycled materials has been found so far.

Despite its benefits for society, the recovery of plastics is a major challenge. Indeed, they are often heavily contaminated after having been in contact with inks, dust, organic and inorganic substances, etc. Today, it is not possible to eliminate this contamination through conventional recycling washing (European Commission, 2019). In the case of polyolefins, the cleaning is reduced to basic hot or cold water washes that are not sufficient to remove contaminants (Horodytska et al., 2020).

These potentially hazardous substances can migrate from the polymer matrix (Geueke, 2018). This is not only of concern in the hygienic packaging sector, but also in the food packaging sector, as the substances can be ingested through food consumption, posing a risk to human health (Lin et al., 2017).

We must highlight the importance of bringing safe recycled plastic to the market. Verifications as to whether contaminants may have been absorbed or formed during the plastic's useful life prior to its recycling must be performed. Knowledge is lacking regarding the contaminants that remain in the polymeric matrix after use or those that can be generated during its reprocessing. This absence of information is currently entailing limitations to its recycling: to solve a problem, one must understand it first.

For this reason, the present work sought to identify the presence of PAHs and POPs in different LDPE matrices retrieved from different recycling processes. These substances may be present in plastic waste and very few publications address the issue of contaminant concentrations in recycled plastic (Conesa et al., 2021).

In addition to quantifying the contaminants mentioned above, this work aims to study the possible origin of these contaminants. The concentration of carbon black and different metals in the samples will thus also be determined. Indeed, the PAHs content could be related to the carbon black present in the samples, as will be shown below.

2. Materials and methods

2.1. Sample collection

The type of polymer used for the analyses was low density polyethylene (LDPE). A total of six LDPE samples from different recycling processes and local recyclers were analysed. Virgin LDPE was collected to compare it with the rest of the samples. All samples were washed and subsequently re-extruded and pelletised. The extrusion temperature varied according to the recycler, ranging from 180 to 210 °C.

The samples were selected according to their origin. On the one hand, *post-industrial LDPE* was used. Its granules were generated from industry-made defective plastic objects and were recycled to be reintroduced into the production processes. Two samples were collected from this type of recycled polymer: the first was plastic reintroduced into the production process, and the second was lower quality plastic, used to produce lower performance items.

We equally selected *post-commercial LDPE*, whose pellets are generated from plastics that do not reach the final consumer. They are mainly used for bags and packaging. This plastic was obtained from a company operating with a patented recycling process, as they remove inks and other impurities from the recycled plastic (EREMA Plastic Recycling).

Finally, samples of *post-consumer recycled plastic pellets*, of two

different origins were used: the first from plastic used in agriculture (such as in greenhouses), and the second from plastic collected from the yellow bin.

All these samples were numbered from one to six and were subjected to the analysis of PAHs, PCDD/Fs and dioxin-like PCBs, and finally metal determination. Prior to the analysis, an amount of approximately 2 kg of the plastic samples collected were crushed using a Retsch model SM 200 cutting mill with a 1.0 mm sieve. For the analysis, different portions of the shredded samples were taken. Table 1 summaries the samples analysed.

2.2. Heavy metals analysis

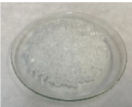
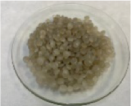
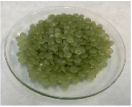



All plastic samples were analysed using a multi-elements standard (Merck-IV 1000 mg/L) for the following metals: Li, B, Na, Mg, Al, Ca, K, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Ag, Cd, In, Ba, Tl, Pb and Bi. Sample digestion was conducted by ultrasonic waves (UW) using 4 mL of HNO₃ (Honeywell Fluka 69%) and with the following programme: 5 min from room temperature to 100 °C; 15 min from 100 °C to 170 °C; 10 min from 170 °C to 240 °C; 15 min isothermally at 240 °C, cooling to room temperature. Upon completion, the samples were filtered (0.45 µm) and diluted to 15 mL with milli-Q water. Finally, the samples were analysed through ICP-MS using Agilent 7700x model equipment.

2.3. PAHs extraction

The compounds to be analysed were obtained from the plastic samples by solvent extraction, adapting the method of Horodytska et al. (2020) in conjunction with the method of Li et al. (2017). The internal standards used to quantify the analysed compounds were added to the samples before extraction (Moreno et al., 2019). To quantify the PAHs, 10 µL of the internal standard MIX 33 2000 µg/mL in Toluene from Dr. Ehrenstorfer-Schäfers was used (additional information on this internal standard has been added in Table S1 in the supplementary material).

To extract the PAHs, a quantity of 2 g of shredded plastic was introduced in a 50 mL vial with a mixture of 30 mL of acetone and

Table 1
Characteristics of the samples used in the present work.

ID	Type	Origin	Treatment	Details	Colour
M1	LDPE	Virgin	–	Transparent	
M2	LDPE	Post-Consumer (Agricultural)	Washed and re-extruded	Brown	
M3	LDPE	Post-Commercial	Attempted treatment	Greenish	
M4	LDPE	Post-Industrial (White)	Washed and re-extruded	Contains inks, white	
M5	LDPE	Post-Industrial (Black)	Washed and re-extruded	Contains inks, black	
M6	LDPE	Post-Consumer	Washed and re-extruded	Contains inks, black	

dichloromethane (1:1 by volume). The vials were closed, and the samples were stirred for 24 h. Once the extraction was completed, the samples were filtered using glass wool as well as sodium sulphate. They were then concentrated using a Fluid Management Systems (FMS) Super-Vap to a final volume of approximately 1 mL. In order to estimate the standard deviation, a new sample of 2 g was used for the analysis.

So as to remove impurities and plastic dissolved during the extraction, all PAHs samples were cleaned up, as performed previously (Li et al., 2017) in the case of some similarly extracted polystyrene samples. The extracts were thus eluted in A C18 SPE cartridges previously conditioned with 5 mL of dichloromethane and 5 mL of hexane. A total of 10 mL of hexane was used to elute the samples.

After the clean-up, all samples were concentrated again using a SuperVap, obtaining a final volume of approximately 1 mL, finally concentrated in vials using a Pasvial evaporator. Immediately prior to the analysis, the ¹³C-isotopically labelled standard was added: 3 µL of anthracene-d10 with a concentration of 2000 µg/mL in dichloromethane for the PAHs samples supplied by AccuStandard Inc., New Haven, CT, USA. To identify and quantify the 16 priority PAHs, the standards established by the U.S. EPA (EPA, 2018) were followed. The analysis of PAHs was performed via high-performance gas chromatography (Agilent 6890 N) with mass spectrometry (Agilent 5973 N) (HRGC-MS).

2.3.1. Carbon black analysis

To check whether there was a relationship between the amount of PAHs analysed in the samples and the carbon black content, it was necessary to determine the black content. The method “Polyolefin pipes and fittings - Determination of carbon black content by calcination and pyrolysis” (International Standard, 2019) was followed.

For the analysis, three sample portions of approximately 1 g (mass m_1) were prepared in three tared crucibles, and this mass was recorded as m_1 . The lidded crucibles were placed with the samples in a muffle furnace under a heating programme of 10 to 15 ± 1 °C/min until a temperature of 550 ± 25 °C was reached. It was allowed to pyrolyze at this temperature for 10 ± 5 min. At the end of the pyrolysis and after a cooling programme of 15 ± 1 °C/min up to 325 ± 25 °C, the crucibles with lids were removed and allowed to cool in a desiccator. They were then weighed every 30 min until constant weighing (this mass was recorded as m_2).

The crucibles without lid were then placed in the muffle furnace and the temperature was set to 900 ± 25 °C. Once this temperature was reached, the crucibles were left to bake for 30 ± 5 min. Finally, the muffle furnace was turned off and allowed to cool until the temperature dropped below 500 °C and the crucibles were removed and placed in a desiccator to cool. The crucibles were weighed every 30 min until constant weight (m_3).

To calculate the carbon black content, expressed as a percentage by mass, the following equation was used.

$$\%CB = \frac{m_2 - m_3}{m_1} \cdot 100$$

2.4. PCDD/Fs and PCBs extraction

The extraction process to analyse the PCDD/Fs and PCBs was the same as that of the PAHs, except that the extractant solvent was replaced with 30 mL toluene, which has previously been shown to be efficient to extract these types of compounds (Wyrzykowska et al., 2009). It is therefore among the most commonly used solvents for POP analysis (Conesa et al., 2021). To analyse the PCDD/Fs, we added to the samples 10 µL of internal standard EPA-1613LCS, and to analyse the dioxin-like PCBs, 10 µL diluted to 200 ppb of WP-LCS, both supplied by Wellington Laboratories.

To purify the PCDD/Fs and PCBs samples, Power-Prep™ equipment from the FMS company was used, which is capable of purifying the

extract automatically. The Power-Prep™ system was programmed to clean the extract using three different columns: a multilayer silica column, where PAHs, phenols, acids and esters, as well as oils and lipids are retained; a basic alumina column, which allows the separation of the fractions of PCDD/Fs and PCBs from other organic compounds and also retains phenols and lipids; and finally, an activated carbon column that allows isolating PCDD/Fs from other organic compounds, as they are retained in the head of the column by its planar configuration, being subsequently eluted in reverse flow. After purification, two fractions were obtained: one containing the PCDD/Fs in toluene and the other containing the PCBs in a mixture of dichloromethane and hexane (1:1 by volume).

After the clean-up, all samples were concentrated in nonane using SuperVap equipment to a final volume of approximately 1 mL and finally concentrated in vials using a Pasvial evaporator. Immediately prior to the analysis, the ¹³C-isotopically labelled standard was added: the 10 µL of EPA-1613ISS solution and 10 µL of WP-ISS solution were diluted to obtain 200 ppb to analyse PCDD/Fs and dioxin-like PCBs respectively, supplied by Wellington Laboratories. The PCDD/Fs and PCBs were identified and quantified via gas chromatography (Agilent 7890B) coupled to triple quadrupole mass spectrometry (Agilent 7010B) (GC-MS/MS) with an automatic injector (Agilent 7693A). Both the list of instrument injection conditions and the method used for data acquisition, Multiple Reaction Monitoring (MRM), for PCDD/Fs and dioxin-like PCBs are shown in Table S2, Table S3 and Table S4 in the

Supplementary Material, respectively.

3. Results and discussion

3.1. Heavy metals

Previous works by Eriksen et al. mention the importance of analysing heavy metals as contaminants in different recycled plastic samples (Eriksen et al., 2018). The present work aimed to find a relationship between the amounts of heavy metals found in the samples and the formation of new contaminants during extrusion, such as PCDD/Fs and dioxin-like PCBs. Indeed, the presence of metals such as copper, iron, zinc or lead can catalyse reactions of formation of these pollutants through de-novo synthesis (Palmer et al., 2021) (Fujimori et al., 2009).

Table S5 shows the results of the metal concentration determination in the plastic samples analysed. It also includes the relative standard deviation (RSD) in percentages calculated for two of the samples (M3 and M6). Table S6 shows each element's limit of detection and quantitation. As can be observed, metal concentrations ranged from 0.00028 mg/kg of Uranium in sample M2, the minimum amount detected, to 1684.75 mg/kg of Aluminium in sample M4.

Among the different metals, those present in most samples and in higher concentration (Fe, Al, Cu, Pb, Zn and Ti) are shown in Fig. 1. As can be observed in Fig. 1, the metal concentrations were higher in samples M4, M5 and M6. These latter samples were recycled through

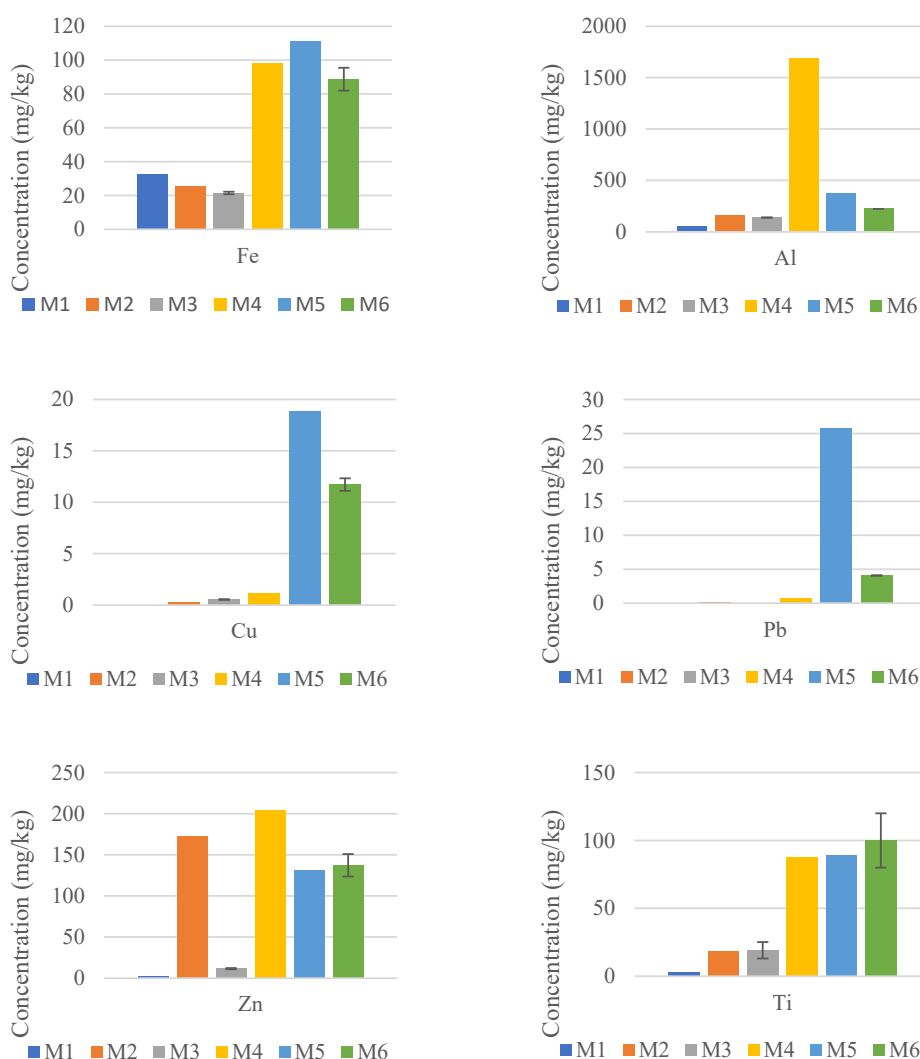


Fig. 1. Contents of the high metal concentrations (>10 mg/kg) in the recycled LDPE samples.

traditional washing, and they were also the dirtiest, as they contained inks and were coloured samples. Of the represented concentrations, the highest was aluminium, which varied between 50.17 mg/kg in sample M1 and 1684.75 mg/kg in M4.

As we discuss these results, we must bear in mind that the metals mentioned above can be present in recycled plastics for different reasons: they can be intentionally added (IAS) as additives and serve as colourants (Ti, Cr, Co, Cd, Pb, Zn, Fe, Al, Cu), or as antioxidants and stabilisers to extend the lifetime of plastics (Cd, Pb, Zn). Others may be unintentionally added substances (NIAS) during their use, deposition and recycling (Fe, Al, Cu, Mn, Zn, Ni) (Hahladakis et al., 2018).

Worthy of note, sample M4 was white, and white pigments usually involve a mixture of aluminium silicate with titanium dioxide. The high concentration may therefore be due to this additive (Inpra Latina (Inpra Latina, 2022)). Ti concentrations ranged from 89.45 mg/kg to 99.97 mg/kg in the dirtiest samples (M5 and M6, respectively) and 87.76 in the white sample (M4).

Regarding the rest of the metal concentrations (As, Cd, Co, Cr, Ni, Mn) (see Figure S1 in the supplementary material), concentrations were below 10 mg/kg. In other words, their concentration can be considered low, but the effect they may have on the recycled plastic should be studied. It is important to remember that some of these metals pose, in themselves, a risk to human health and the environment. The following are classified as mutagenic, carcinogenic, toxic to reproduction and hazardous to the environment: As, Cd, Co, Cr, Pb, Sb, Ti. No Sb was found in any of the samples analysed. As in the case of the metals shown in Fig. 1, the concentrations of metals in Figure S1 also tended to present higher concentrations in samples M4, M5, and M6.

3.2. PAHs and carbon black content

As mentioned above, the analysis of the 16 priority PAHs was performed on a total of 5 samples of recycled LDPE from different recycler. This implies recycling process differences, for example during polymer washing. Therefore, for comparison purposes, we also analysed a sample of virgin LDPE.

In order to check the quality of the obtained results, the recoveries of

all the deuterated congeners were calculated. Recoveries of between 50 and 140% were found, the lowest being obtained for the congeners with the highest volatility and the highest for those with the lowest volatility. All, however, were within the admissible range of recoveries stipulated by the EPA (EPA, 2018). Furthermore, as an additional control measure, two duplicates were performed, one for the cleanest sample (M3) and one for the dirtiest sample (M6). Standard deviances were calculated for all congeners. These results can be found in Table S7 in the supplementary material.

The results of the PAH concentrations found in the samples are presented in Fig. 2. A detailed description of the PAH concentrations is provided in tabular form in the supplementary material (Table S7 in the supplementary material). Fig. 3 presents a graph showing the sum of the 16 priority PAH congeners analysed, allowing to compare the PAH contamination of all the samples.

As illustrated in Fig. 3, the sum of the concentrations of the 16 priority PAHs varied from 123.94 ng/g in the sample with the lowest

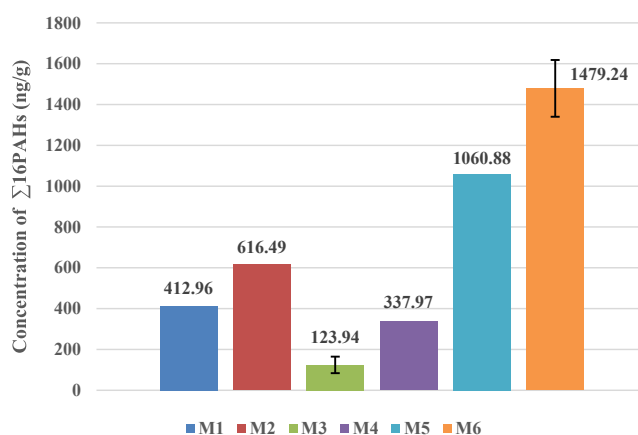


Fig. 3. Sum of PAHs concentration in the different recycled and virgin LDPE samples.

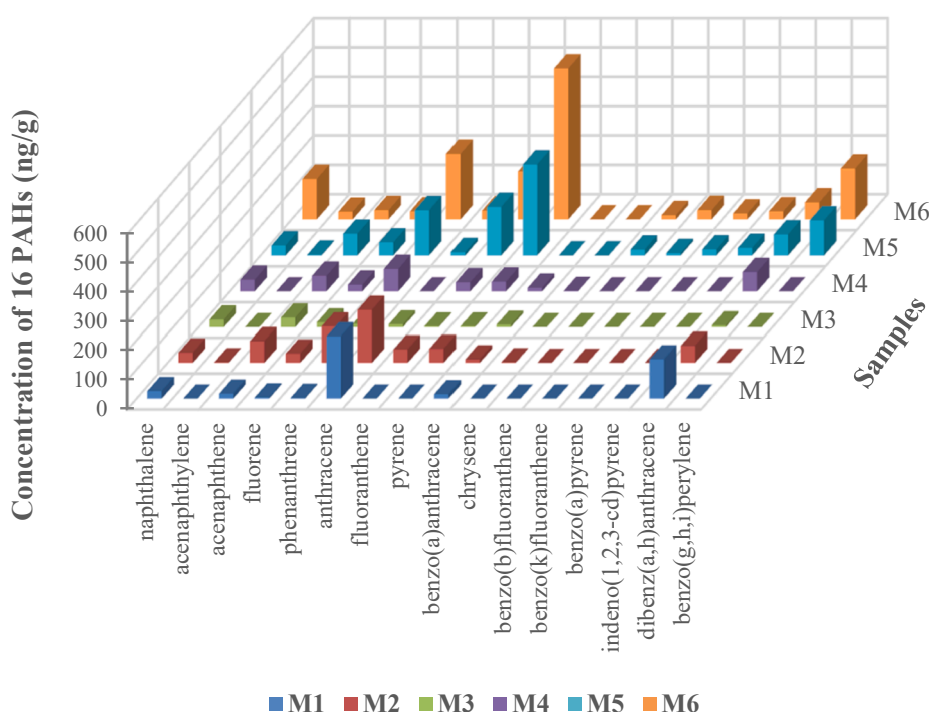


Fig. 2. Polycyclic aromatic hydrocarbon contents in the recycled LDPE samples and comparison with virgin LDPE.

concentration (M3), to 1479.24 ng/g in the sample with the highest concentration (M5).

The results obtained indicate that, as expected, the highest PAHs concentrations were present in samples M5 and M6. In both cases, the congener found in greater quantity was pyrene, with a concentration of 309.74 ng/g in sample M5 and 514.41 ng/g in sample M6. As mentioned above, these two samples are black. This may be due to the fact that during the recycling, the plastic is mixed with carbon black, which is used as a thermal stabiliser in recycled LDPE (Peña et al., 2001). The concentration of pyrene in these samples could therefore be related to the amount of carbon black in the sample. Locati et al. (1979) conducted a study in which they analysed the 16 priority PAH congeners in different carbon black samples and found higher concentrations of pyrene compared to the other PAHs—up to 430 µg/g in these samples.

In addition to the data found in the literature, the carbon black content in the black samples was analysed to reinforce the claim of a possible relationship between PAHs content and Carbon Black. The analysis resulted in a content of 2.00 ± 0.44 % carbon black for sample M5, and 1.51 ± 0.40 % for sample M6.

The concentrations obtained for all the PAHs were higher in most cases than the mean concentrations found in other types of plastic, such as polystyrene [nd – 273 ng/g] (Li et al., 2017). Moreover, Bouhroum et al analysed PAH concentrations in North Atlantic gyre plastic debris and found PAHs concentrations in polyethylene samples [nd – 98.0 ng/g]

(Bouhroum et al., 2019).

Unexpectedly, the concentrations in samples M3 and M4 were lower than those in the virgin LDPE. The PAH concentration in sample M3 was 2.5 times smaller than in the virgin LDPE (sample M1) and 1.2 times smaller in the case of M4. This may be due to the efficiency of the washing processes of the recycling companies that provided the samples. The concentration of PAHs in sample M2 presented expected values: they were higher than that of the cleanest samples (M1, M3, M4) but lower than that of the dirtiest samples (M5, M6). The reason may be, as already mentioned, that M2 is an agricultural recycled plastic that is constantly exposed to the elements and to the combustion gases of circulating vehicles.

3.3. PCDD/Fs and PCBs

The results obtained for the recoveries of the ¹³C-labeled PCDD/Fs standards were all within the acceptable EPA 1613 ranges (Agency, 1994) (Table S8): 30% to 102% recovery for all congeners. Likewise, the recoveries of PCBs were within the acceptable EPA 1668 ranges (EPA, 2008) (Table S9), i.e., a 36% to 122% recovery. As in the case of the PAHs, the cleanest (M3) and dirtiest (M6) samples regarding PCDD/Fs and dioxin-like PCBs were replicated and the standard deviation was calculated (results can be found in Table S10 in the supplementary material).

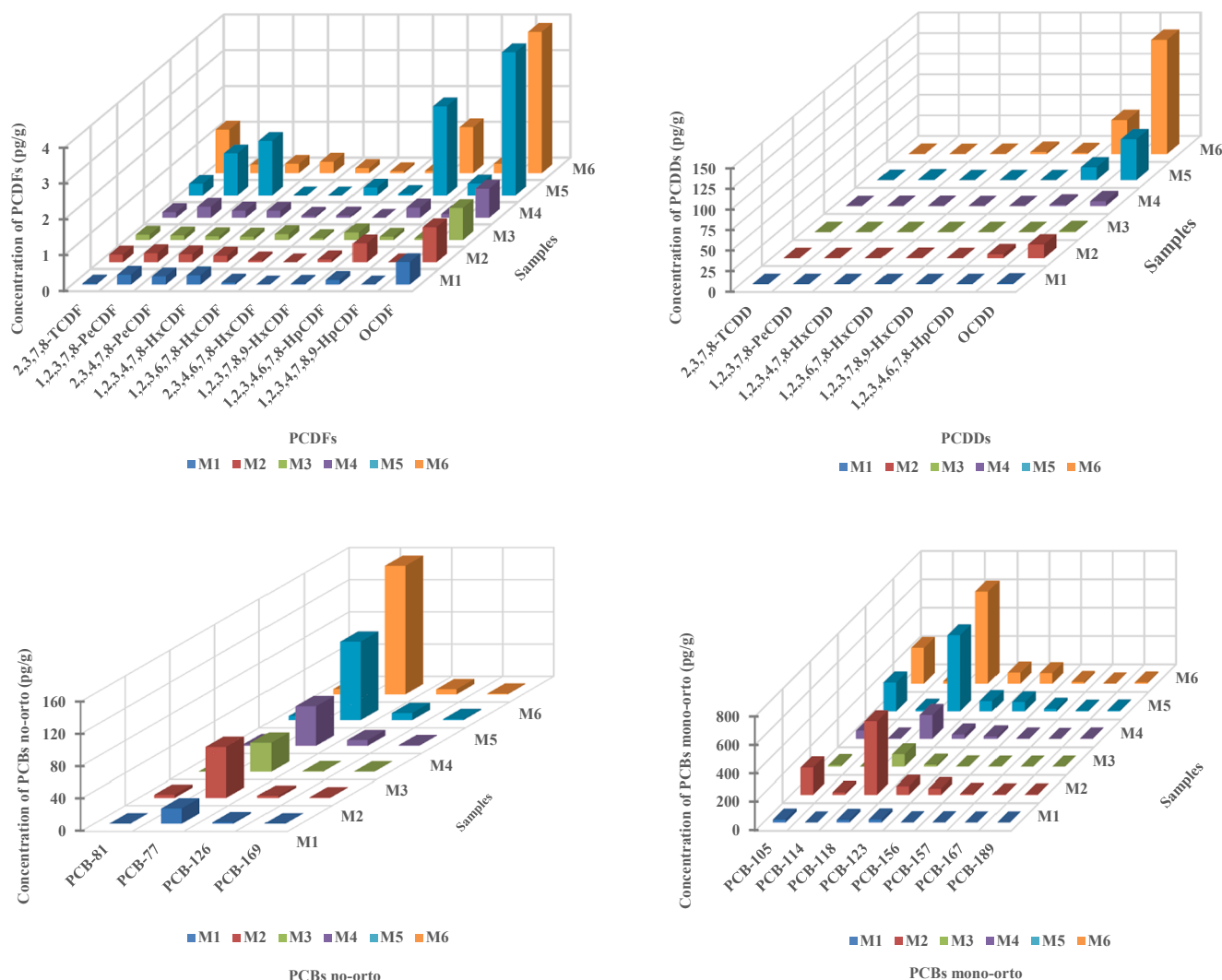


Fig. 4. PCDDs, PCDFs and PCBs content in the recycled and virgin LDPE samples.

The results obtained for the concentrations of the different congeners of PCDD/Fs and PCBs are presented in Fig. 4 and a more detailed description can be found in Table S10 (supplementary material).

The reported data for PCDD/Fs and PCBs includes the specific congener results. In addition, as proposed by the World Health Organization (WHO) and the United Nations Environment Programme (UNEP), Toxic Equivalency Factors (TEF) were applied, using the WHO₂₀₀₅-TEF values (Van den Berg et al., 2013) to determine the samples' total Toxic Equivalency (TEQ).

Table S10 in the supplementary material shows that the concentrations obtained for PCDD/Fs congeners were between [nd – 139 pg/g] and the concentrations for PCBs congeners between [0.19–649 pg/g], PCB concentrations being higher in all the samples.

The different samples' total toxicity was evaluated and the toxic equivalents per sample gramme were evaluated. The results are illustrated in Fig. 5. This is of notable importance. Indeed, the fact that a sample presents higher concentrations after adding the different congener concentrations does not imply that the sample is more toxic. This is because the WHO has assigned a different toxicity weight to each congener (Van den Berg et al., 2013). In the samples analysed, M6 presented a higher total concentration of congeners, but M5 was ultimately the most toxic of all.

The analysis performed shows that, based on the analysis of PCDD/Fs, the most contaminated samples were M5 and M6 (Fig. 4). With respect to PCBs, as in the case of PCDD/Fs, M5 and M6 samples were found to be the most affected as well. Worthy of note, no difference as pronounced as that of PAH content was observed for PCDD/Fs, nor for PCBs.

No study was found in the literature on the presence of PCDD/Fs or dioxin-like PCBs in samples of plastic waste or recycled plastic. The present work therefore provides important information regarding the potential concentrations of these contaminants in recycled plastics. We did encounter a study (Bouhroum et al., 2019), however, that analysed other, less toxic, PCB congeners. In the study, two of the examined PCB congeners coincided with the objects of study in the present work. The determined concentrations were [nd – 10.2 ng/g] for PCB-77 and [nd – 7.9 ng/g] for PCB-105. These values are very high compared to those found in the recycled plastic of the present work for these congeners: PCB-77 [18.7–159.6 pg/g] and PCB-105 [11–253 pg/g], which were 1000 times lower.

Another notable issue that we addressed was whether PCDD/Fs could possibly be formed during the plastic extrusion process via de-novo synthesis, since the extrusion temperature of thermoplastic polymers such as LDPE ranges between 180 °C and 210 °C. Therefore, the metal concentrations involved in the de-novo synthesis (Fe, Zn, Pb, Cu) were analysed.

Different correlations were tested, and a good agreement ($R^2 > 0.99$)

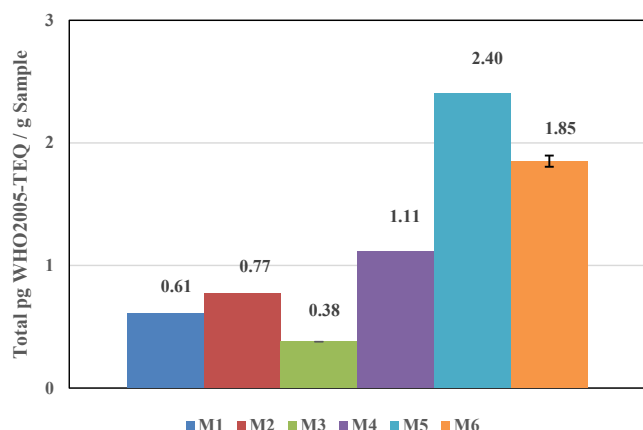


Fig. 5. Dioxin-like total toxic content of the recycled LDPE samples.

was found between the concentration of copper and that of furans, and with the samples' total dioxin toxicity ($R^2 = 0.95$). The correlation with other metals such as Fe, Ti or Zn presented much lower R^2 values. Figure S2 in the supplementary material shows the relationship between copper (involved in de-novo synthesis) and the concentration of PCDD/Fs and dioxin-like PCBs.

Another important fact concerning the origin of the chlorinated pollutants was the PCDD/Fs congener profile present in the samples. In this sense, the fact that the de-novo route produces many more furans than dioxins is well known (Fiedler et al., 2000; Huang and Buekens, 1996). Fig. 6 show the results of the analysis of PCDD/Fs profiles of all six samples.

This Figure shows that dioxin concentration was much higher than that of furans, and because of that, the de-novo route was ruled out. A profile comparison among different samples presented similarities with urban air samples from different environments, in particular with samples collected in the same geographical area (Aristizábal et al., 2011; Conesa and Gálvez, 2006). This demonstrates that the origin of dioxin-like compounds can be associated with contact with ambient air, or with the environment generally, as these samples were exposed to it. The absorption of PCDD/Fs by plastics was in fact observed a long time ago (Kreisz et al., 1997). The degree of absorption was in fact such, that the authors proposed a system to reduce emissions in a plastic waste incineration plant.

In the urban air samples, the four major congeners were [1,2,3,4,6,7,8-HpCDF], [OCDF], [1,2,3,4,6,7,8-HpCDD] and [OCDD], as in the profiles of samples M2, M4, M5 and M6. With respect to samples M1 (virgin LDPE) and M3, the congener concentrations found in these samples were very low (<1 pg/g) and their profiles did not coincide with the PCDD/F profile in urban air. They were, however, very similar, demonstrating that the M3 sample's cleaning process leaves the sample almost in its original state before recycling (M1).

4. Conclusions

The objectives of this work were to analyse samples of recycled plastic from different sources, searching for contaminants that are toxic to human health and hazardous to the environment, and to try to find out their possible origins.

Low amounts of heavy metals, PAHs and POPs (PCDD/Fs and dioxin-like PCBs) were found in all samples. The study of these contaminants showed concentration differences according to the origin and cleaning process applied to the plastic during its recycling.

The highest PAH concentrations were found in the two dirtiest samples (cleaned with basic washing processes such as hot and cold water) M5 and M6. The M3 sample, however, which had been washed more exhaustively, presented a PAHs concentration that was lower than that found in the virgin polymer. One of the PAHs found in major quantities in the black samples (Pyrene) is likely to come from one of the additives used in the black samples, carbon black. Indeed, Pyrene has previously been shown to be present in high concentrations in carbon black samples (430 µg/g). Therefore, an analysis of carbon black was performed to demonstrate carbon black presence in the black samples. And it was found that the additive was present in both black samples M5 and M6, in percentages of 2.0% and 1.5%, respectively.

With respect to the persistent organic pollutants, toxicity was found to vary from 0.38 pg WHO2005-TEQ/g sample to 2.40 pg WHO2005-TEQ/g for the most toxic sample. As expected, the dirtiest samples had the highest toxicity values. Furthermore, it is worth noting that the lowest toxicity value was not found in the virgin plastic sample (M1) but in sample M3, a sample that underwent a thorough washing by the recycling company. This finding underlines the importance of the washing stage of recycling processes.

With regard to the origin of the POPs, an attempt was made to find possible correlations with the analysed metals. Indeed, it has been shown that under certain temperatures, metals such as iron, copper, zinc

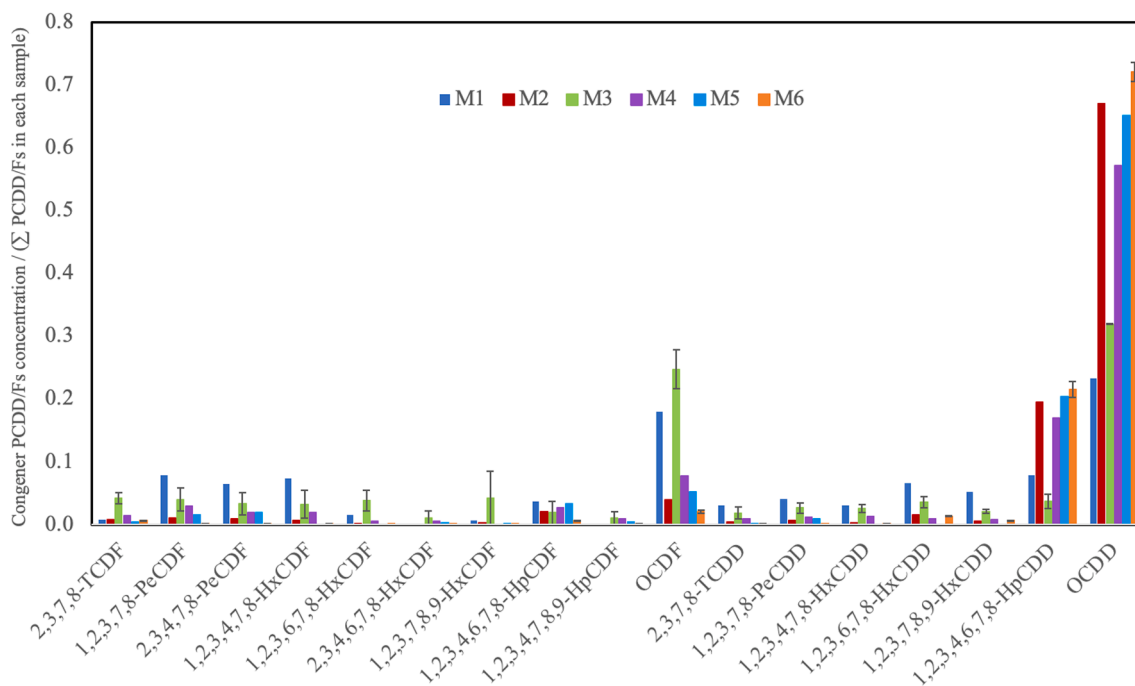


Fig. 6. PCDD/Fs concentration profiles, shown as the concentration of each congener divided by the sum of PCDD/Fs in each sample.

or lead can catalyze the formation of PCDD/Fs and dioxin-like PCBs, and when working with recycled plastics, the extrusion processes can reach temperatures of up to 210 °C for LDPE. Therefore, different correlations between metals and sample toxicity were studied. A linear relationship was found between the amount of copper present in the samples and their toxicity.

However, this argument has not been regarded as strong enough to account for the origin of the pollutants, so different profiles of PCDD/Fs in different types of samples were compared with congener profiles available in the literature. A very significant coincidence of profiles with samples of urban air was found. Therefore, the possible origin of PCDD/Fs and dioxin-like PCBs is the absorption of these compounds present in urban air.

As a general conclusion, we demonstrated the importance of monitoring the presence of these pollutants in samples of recycled plastics and additives, as they may be a source of unwanted toxic pollutants. We also showed the relevance of monitoring the washing processes of recycling companies. Indeed, concentration levels of these pollutants were found to be similar to, or even lower, in the sample having undergone an exhaustive washing process than that found in the virgin plastic sample.

In this way, samples M2 and M3 could be used for any type of application, including in contact with food, while other samples such as M5 or M6 should be used for less demanding applications such as the manufacturing of pots, rubbish bags or similar products.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Ministry of Science and Innovation (Spain) [grant number PID2019-105359RB-I00], and by the University of Alicante [grant number UAUSTI21-03].

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2022.03.016>.

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